



DEPARTMENT OF HEALTH & HUMAN SERVICES  
Public Health Service

Agency for Toxic Substances  
and Disease Registry  
Atlanta, GA 30333



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Dear Ms. Newton and Mr. Reetz:

We are writing to inform you of the finding of a public health hazard associated with community exposures to hydrogen sulfide air emissions from the Excel Dairy, Excel Township, Marshall County, Minnesota (near Thief River Falls, MN). This conclusion is based on air monitoring data collected by the Minnesota Pollution Control Agency (MPCA) and by the Agency for Toxic Substances and Disease Registry (ATSDR) during an Exposure Investigation (EI). A more formal and complete Exposure Investigation report, including more detailed descriptions of methodologies and results, will be available later this year.

#### Background

The Excel Dairy under the ownership of The Dairy Dozen of Veblen, South Dakota has been permitted since 2006. The Dairy has a capacity of 1544 animal units or 1100 cows over 1,000 pounds (milked or dry) (Permit MN0068594). The Dairy has 3 free-stall barns, a sand separator building, a feed storage pad, and 3 earthen manure storage basins or lagoons. The lagoons are either uncovered or incompletely covered, and are thought to be the major source of odors and emitters of hydrogen sulfide (H<sub>2</sub>S) at the facility. Approximately 12 families live within 1 mile of the Excel Dairy.

The Minnesota Department of Health (MDH) and the Minnesota Pollution Control Agency (MPCA) received complaints from citizens about odors, health effects and hydrogen sulfide (H<sub>2</sub>S) emissions originating at the Dairy. Citizen health complaints included upper respiratory effects (such as nasal congestion and sore throats), itchy eyes, trouble breathing, nausea and headaches.

In response to these complaints, MPCA installed two continuous air monitors (CAMs) at the fence line to the northeast (May 6, 2008) and to the west (May 19, 2008) of the on-site manure lagoons at Excel Dairy. MPCA also installed meteorological equipment at the northeast site. Figure 1 shows the relationship of MPCA air monitoring equipment to the Dairy. Since the range of the MPCA H<sub>2</sub>S monitors were from 0-90 ppb, air concentrations in excess of 90 ppb could not be quantified. As a result, the maximum concentrations at those locations are unknown.

Minnesota Ambient Air Quality Standards (MAAQS) require that there be no more than two 30 minute periods of H<sub>2</sub>S above 30 ppb in 5 days, or no more than two 30 minute periods of H<sub>2</sub>S above 50 ppb in any year (Minnesota Administrative Rules 7009.0080). Standards are applicable at the property boundary of the facility, and/or at locations to which the general public has access. Large livestock facilities are exempt from these requirements for a maximum of 21 days per calendar year during and for 7 days after manure is removed from barns or manure storage facilities. Operators of livestock facilities claiming this exemption are required to provide notice to either the MPCA or the county feedlot officer. The MPCA may not require air emissions modeling for a type of livestock system that has not had a hydrogen sulfide emission violation (Minnesota Statutes 116.0713). MDH has promulgated a subchronic Health Risk Value (HRV) for hydrogen sulfide of 7 ppb for a period of 13 weeks (Minnesota Administrative Rules 4717.8000-4717.8600).

Over a 4 month period (May-Sept), MPCA monitoring data showed the hydrogen sulfide levels exceeded 30 ppb for 15.5 hours (cumulative) at the northeast monitor location and for 172.5 hours (cumulative) at the west monitor location. Furthermore, despite the fact that the maximum concentrations for the MPCA data are not known, the average concentration over that period exceeded the subchronic HRV of 7 ppb.

The Minnesota Attorney General and the MPCA filed an Interim Order for injunctive relief against the Excel Dairy owner on June 20, 2008 to address operational shortfalls contributing to these ambient releases of hydrogen sulfide. As you are aware, these exceedences also prompted the Notice of Violation issued by USEPA to Excel Dairy owners on July 18, 2008.

#### Toxicity of Hydrogen Sulfide

Of all of the chemicals that are emitted from the storage, handling, and decomposition of animal wastes, hydrogen sulfide is one of the most important. This is due to the fact that large amounts of hydrogen sulfide gas are produced under anaerobic conditions and that is a gas that is heavier than air. As a result, it has the ability to accumulate in low-lying areas and when meteorological conditions lead to less air mixing. The odor threshold for hydrogen

sulfide ranges from 0.5 to 300 ppb. Adverse health effects associated with short-term exposures to hydrogen sulfide include airway constriction in individuals who have asthma, decreased lung function, eye irritation, dizziness, nausea, and headache. Acute exposures to high concentrations (greater than 100 ppm) may result in pulmonary edema, physical collapse, and death (ATSDR, 2006). Although many of these effects from acute exposure are reversible, exposure to high concentrations for even a short period can lead to long-lasting neurological impacts.

Long-term or repeated episodic exposures to hydrogen sulfide are likely to result in the same types of reversible effects observed with acute exposures, such as irritation of nose and respiratory tract, headaches and nausea (cf. MDH, 2008, Collins and Lewis, 2000). There is only limited epidemiological data assessing the potential for irreversible effects from chronic exposures low level (below 1 ppm). However, several studies and case reports have observed neurological effects with such low level exposure (ATSDR, 2006).

#### ATSDR Exposure Investigation

A group of citizens acquired a Jerome 631-X meter (instrument for measuring hydrogen sulfide in air), and developed a protocol to document readings of hydrogen sulfide. This citizen group submitted data to MDH, showing many periods of hydrogen sulfide in the hundreds of parts per billion (ppb), and on one occasion citizens submitted data with periods in excess of 1,000 ppb of H<sub>2</sub>S. These detections were reported as various locations near residences and areas outside of the Excel facility.

Based on a request from MDH to collect more data about community exposures to hydrogen sulfide, ATSDR approved the request for an Exposure Investigation (EI) on June 19, 2008. On July 9, 2008, ATSDR staff initiated sampling for hydrogen sulfide levels at three residential locations in proximity to the Excel Dairy (Figure 1). The sampling instruments, known as Single Point Monitors, were placed at both outdoor and indoor locations at these locations. The monitors detected the concentration of hydrogen sulfide continuously throughout the day for a 2-3 week period at each location. In addition, the two MPCA monitoring stations continued to collect data during the ATSDR EI at the fence line to the northeast and west of the onsite manure lagoons.

Although hydrogen sulfide is the target contaminant for the EI, it is acknowledged that over 80 chemicals are known to be emitted to air from dairy operations. In addition to hydrogen sulfide, chemicals that could contribute to odors and irritation include ammonia and other reduced sulfur compounds including dimethyl sulfide and dimethyl disulfide (Filipy et al., 2006).

#### Results from EI

In addition to the MPCA air standard for hydrogen sulfide (no more than two 30 minute periods of H<sub>2</sub>S above 30 ppb in 5 days, or no more than two 30 minute periods of H<sub>2</sub>S above 50 ppb in any year), the air monitoring data were compared to the ATSDR Minimal Risk Levels (MRLs) for acute or intermediate exposures. The acute MRL for hydrogen sulfide

exposure is 70 ppb is based on respiratory effects in humans resulting from a 30 minute exposure. The intermediate MRL is 20 ppb, based on neurological effects in animals resulting from exposure over a 10 week period. Other comparison criteria are summarized in Table 1. Background concentrations of hydrogen sulfide in outdoor air are typically less than 1 ppb (ATSDR, 2006).

The data indicate that both ATSDR and MPCA health based guidelines were exceeded at all five ATSDR and MPCA sampling locations. At ATSDR sampling locations S1 and S3, where monitoring occurred over a 15 day period from July 16-July 31, ambient air concentrations reached levels up to 481 ppb, with many periods where air concentrations were over 100 ppb. Furthermore, many of these episodes of elevated hydrogen sulfide concentrations lasted for many hours. During a two week period, ambient concentrations of hydrogen sulfide at Site 3, the residence in closest proximity and most affected by site releases, exceeded the acute ATSDR MRL for over 8 hours (cumulative), but the average concentration over that time did not exceed the intermediate ATSDR MRL.

During this same period, the 30 min average concentrations at the MPCA Site 2 monitor (west of facility and closest to the manure lagoons) exceeded the acute ATSDR MRL for 10.5 hours. The MPCA air quality standards for H<sub>2</sub>S were exceeded over 300 times at the MPCA monitoring stations before, during, and after the EI (May-Sept). Comparison of the MPCA data to longer duration criteria (e.g. ATSDR Intermediate MRL) is limited because the maximum concentrations were not quantifiable with their monitoring.

### Child Health Considerations

Citizens have reported the presence of children on the Dairy site. During the EI, ATSDR and MDH staff noticed a toddler onsite in at a mobile home. It is unknown whether or not workers and their families live onsite. Manure lagoons are unrestricted and easily accessible to workers and their families. Therefore, children living on or near this site may be at risk for elevated exposures to hydrogen sulfide.

### Conclusions

Although ATSDR did not conduct a formal health study to evaluate the health of people living on or near Excel Dairy, the symptoms described by the residents to ATSDR and MDH staff were consistent with the known acute health effects of hydrogen sulfide exposure. Based on the air monitoring data collected by during the EI and by MPCA, ATSDR and MDH conclude that inhalation exposure to hydrogen sulfide poses a public health hazard to area residents.

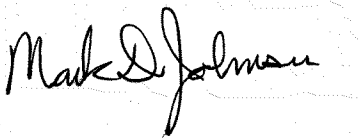
No data has been provided to ATSDR or MDH to determine the concentration of hydrogen sulfide exposure that individuals who work or live on the Excel Dairy property may experience. However, given their proximity to the source of emissions, the exposure of these individuals may be a significant health concern.

## Recommendations

- 1) Excel Dairy should take action immediately to implement improved emission control measures that will significantly reduce the levels of exposure to hydrogen sulfide gas released from onsite operations.
- 2) MPCA and Excel Dairy should coordinate to implement an air monitoring program to verify the effectiveness of emission control measures in reducing the release of hydrogen sulfide gas.
- 3) Excel Dairy should restrict access to lagoons to reduce physical hazards and direct exposures to trespassers and children living on-site.

ATSDR and MDH are available to consult further with U.S. EPA and MPCA on remediation efforts at this site. If you have any questions, please contact Mark Johnson at the ATSDR Region 5 Office (312-886-0840) or Rita Messing at MDH (651-201-4916).

Sincerely,



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The Dairy Dozen

### References

ATSDR, 2006. Toxicological Profile for Hydrogen Sulfide. Agency for Toxic Substances and Disease Registry, Atlanta, GA.

Collins, JD and D Lewis, 2000. Hydrogen Sulfide: Evaluation of Current California Air Quality Standards with Respect to Protection of Children. California Air Resources Board, California Office of Environmental Health Hazard Assessment.

Filipy, J. et al., 2006. Identification and quantification of volatile organic compounds from a dairy. Atmospheric Environment 40: 1480-1494.

MDH, 2008. Memo from Rita B. Messing to John Linc Stine.

Table 1: Guidelines for hydrogen sulfide exposures

	Exposure Value	Exposure Period/Intent
State of Minnesota	30 ppb, no more than twice in 5 days	Ambient Air Quality Standard, not to be exceeded except for exceptions noted in Minnesota Laws.
State of Minnesota	50 ppb no more than twice per calendar year	Ambient Air Quality Standard, not to be exceeded except for exceptions noted in Minnesota Laws.
ATSDR	70 ppb	Acute Minimal Risk Level—value for up to 14 days of exposure. Exposures below this value are not expected to result in non cancerous adverse health effects
ATSDR	20 ppb	Intermediate Minimal Risk Level—value for between 15-365 days of exposure. Exposures below this value are not expected to result in non-cancerous adverse health effects
State of Minnesota	7 ppb	Health Risk Value (HRV) — Subchronic exposure (up to 13 weeks)
California EPA	30 ppb	Reference Exposure Limit (REL) —Acute exposure, up to 1 hr
AIHA	100 ppb	ERPG-1—The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor
USEPA	1.4 ppb	Reference concentration (RfC): concentration for a substance in air that EPA considers unlikely to cause noncancer health effects over a lifetime of chronic exposure.
WHO	14 ppb	Medium-term tolerable concentration: The level at which exposure could occur for up to 90 days without appreciable risk of adverse health effects.

Figure 1. Excel Dairy with ATSDR and MPCA Monitoring Stations.





Figure 2: Data trends for most adversely affected ambient air during the ATSDR Exposure Investigation- Residential Monitoring Site 3

